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TECHNICAL REPORT

Aluminum Micro-Balloons as Improved Fuel for Warhead Explosives

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UNIT CONVERSION TABLE
U.S. customary units to and from international units of measurement*

U.S. Customary Units	Multiply by ← Divide by [†]	International Units
Length/Area/Volume		
inch (in)	2.54 $\times 10^{-2}$	meter (m)
foot (ft)	3.048 $\times 10^{-1}$	meter (m)
yard (yd)	9.144 $\times 10^{-1}$	meter (m)
mile (mi, international)	1.609 344 $\times 10^3$	meter (m)
mile (nmi, nautical, U.S.)	1.852 $\times 10^3$	meter (m)
barn (b)	1 $\times 10^{-28}$	square meter (m^2)
gallon (gal, U.S. liquid)	3.785 412 $\times 10^{-3}$	cubic meter (m^3)
cubic foot (ft^3)	2.831 685 $\times 10^{-2}$	cubic meter (m^3)
Mass/Density		
pound (lb)	4.535 924 $\times 10^{-1}$	kilogram (kg)
unified atomic mass unit (amu)	1.660 539 $\times 10^{-27}$	kilogram (kg)
pound-mass per cubic foot ($lb\ ft^{-3}$)	1.601 846 $\times 10^1$	kilogram per cubic meter ($kg\ m^{-3}$)
pound-force (lbf avoirdupois)	4.448 222	newton (N)
Energy/Work/Power		
electron volt (eV)	1.602 177 $\times 10^{-19}$	joule (J)
erg	1 $\times 10^{-7}$	joule (J)
kiloton (kt) (TNT equivalent)	4.184 $\times 10^{12}$	joule (J)
British thermal unit (Btu) (thermochemical)	1.054 350 $\times 10^3$	joule (J)
foot-pound-force (ft lbf)	1.355 818	joule (J)
calorie (cal) (thermochemical)	4.184	joule (J)
Pressure		
atmosphere (atm)	1.013 250 $\times 10^5$	pascal (Pa)
pound force per square inch (psi)	6.984 757 $\times 10^3$	pascal (Pa)
Temperature		
degree Fahrenheit ($^{\circ}\text{F}$)	$[\text{T}({}^{\circ}\text{F}) - 32]/1.8$	degree Celsius (${}^{\circ}\text{C}$)
degree Fahrenheit ($^{\circ}\text{F}$)	$[\text{T}({}^{\circ}\text{F}) + 459.67]/1.8$	kelvin (K)
Radiation		
curie (Ci) [activity of radionuclides]	3.7 $\times 10^{10}$	per second (s^{-1}) [becquerel (Bq)]
roentgen (R) [air exposure]	2.579 760 $\times 10^{-4}$	coulomb per kilogram ($C\ kg^{-1}$)
rad [absorbed dose]	1 $\times 10^{-2}$	joule per kilogram ($J\ kg^{-1}$) [gray (Gy)]
rem [equivalent and effective dose]	1 $\times 10^{-2}$	joule per kilogram ($J\ kg^{-1}$) [sievert (Sv)]

* Specific details regarding the implementation of SI units may be viewed at <http://www.bipm.org/en/si/>.

[†]Multiply the U.S. customary unit by the factor to get the international unit. Divide the international unit by the factor to get the U.S. customary unit.

Objective.

To show that it is feasible for shock compressed aluminum particle/water mixtures to release energies comparable to those in current aluminized explosives with the goal of enhancing blast waves. This 6.2 grant work provides the baseline technology to understand shock wave experiments done and to be done on this Al/water mixture. Subject matter expertise in shock wave compression of condensed matter and detonation physics has been a major component of the analysis work accomplished in the present research

Previous studies suggest that metal/water reactions are possible over a range of different timescales. Mixtures of aluminum and ice have been shown to burn on timescales consistent with propellant applications [1]. Shidlovskij [2] has published a paper in which aluminum and water were made to react using an explosively-generated shock wave. While these papers suggest that metal/water reactions can occur on fast timescales, it is clear that more study is needed to determine if this reaction can be understood from a shock wave compression viewpoint. Such analysis will allow future experiments to be designed to obtain data that define air blast energy release models. This was to determine the feasibility of Aluminum/water mixtures use to achieve DTRA's enhanced blast wave goals.

If aluminum/water samples can be made to react fast under shock compression, large power will be produced in reactive shock waves transmitted through the mixture. The three issues addressed in this grant are varying the initiation threshold, changing the speed of the fast reaction and designing a shock wave system to reach the high ignition pressures required by this low impedance material. To accomplish these goals requires knowing the unreacted Hugoniot [thermodynamic end states] of this mixture and having a one-dimensional strain shock wave system that creates a shock pressure of several kbar in the mixture . It is also necessary to have techniques that change the rate of energy release in order to design shock wave experiments that allow understanding of the mechanisms occurring and driving the reactions.

Therefore, three critical subjects will be treated in separate sections of unreacted Hugoniot, techniques to change the reaction rate and shock wave driver systems to reach the expected high pressures required for inducing this reaction were worked on.

Unreacted Hugoniot of multi-component mixtures

The mixture laws reviewed by Petel and Jette [3] showed that the one based on kinetic energy averaging (KEA) was the best to compute the inert Hugoniot for a 50/50 wt % Al/H₂O mixture. The KEA mixture method assumes pressure equilibrium and therefore the mixtures equilibrium particle velocity is determined from the particle velocity of each component at a given equilibrium P where

$$u(P)_{mix}^2 = \sum_k Y_k u(P)_k^2$$

Y_k is the mass fraction of the material. This relationship is a generalization of the KEA

method to allow more than two components in the mixture. The component Hugoniots used are:

$$\begin{aligned} U &= 0.535 \text{ cm}/\mu\text{s} + 1.34 u & (24 \text{ ST aluminum, Ref. 4}) \\ U &= 0.1483 \text{ cm}/\mu\text{s} + 1.099 \ln(1+u/0.519) & (\text{water, } P < 0.25 \text{ Mb, Ref. 5}) \\ U &= 0.55 \text{ cm}/\mu\text{s}; \text{ elastic shock velocity} & (\text{borosilicate glass } < 0.2 \text{ Mb, Ref. 4}) \end{aligned}$$

The initial density of the mix is $\rho_{0 \text{ mix}} = 1/v_{0 \text{ mix}}$ where

$$v_{0 \text{ mix}} = \sum_k Y_k v_k(P=0)_k$$

The $v_{0 \text{ mix}} = 0.67659 \text{ cm}^3/\text{g}$ since $v_{0 \text{ Al}} = 0.37037 \text{ cm}^3/\text{g}$, $v_{0 \text{ water}} = 1 \text{ cm}^3/\text{g}$, and Borosilicate glass for micro-balloons has $v_{\text{glass}} = .38462 \text{ cm}^3/\text{g}$ for a 48.5/48/5/3 Wt % mixture.

For every $u_{\text{mix}}(P)$ value the shock velocity of the mixture is obtained from single shock momentum jump equation

$$U_{\text{mix}} = P_{\text{mix}} / [\rho_{0 \text{ mix}} * u_{\text{mix}}]$$

Now the volume at P_{mix} is found using the single shock mass jump equation

$$v_{\text{mix}}(P_{\text{mix}}) = (U_{\text{mix}} - u_{\text{mix}})/U_{\text{mix}}$$

Therefore, a P-v Hugoniot for the non-porous mixture is known from this last equation.

The Hugoniot for this mixture with porosity can be obtained from the Grueneisen equation of state [6]. The porous Hugoniot point for the same volume has to be higher due to the added thermal energy that the porosity provides when these pores are totally collapsed by the shock wave. The equation relating the Hugoniot of the non-porous mixture to a porous one is

$$P(v)_H^{\text{porous}} = P(v)_H^{\text{solid mix}} \left[\frac{1 - \frac{\gamma_0}{2v_0} (v_0 - v)}{1 - \frac{\gamma_0}{2v_0} (v_{00} - v)} \right]$$

where v_0 is initial $v_{0 \text{ mix}}$, γ_0 is Grueneisen constant for non-porous mix, and v_{00} is the initial volume of the porous mixture that is obtained from the reciprocal of its measured initial density. The γ_0 for the mix if interfacial energies can be ignored is [7]

$$\gamma_o = \sum_k Y_k \gamma_k(P=0)_k$$

which is just the mass average sum of the γ 's for each constituent. Although not totally true the $\gamma_o/v_{0 \text{ mix}}$ is assumed to be constant since its variation with change in v is not known. Note that this is a commonly made assumption in the field of shock waves. This porous P-v Hugoniot can be converted into a more useable P-u form by the equation obtained from the conservation of mass and momentum equations resulting in

$$u^{porous} = \sqrt{P(v)_H^{porous}(v_{oo} - v)}$$

$$U^{porous} = v_{oo} \sqrt{\frac{P(v)_H^{porous}}{(v_{oo} - v)}}$$

The (U, u) data points for the inert Hugoniot of 50/50 % by weight with 20% can be fitted by a second order polynomial

$$U^{porous} = 0.0471 \text{ cm}/\mu\text{s} + 3.3854 u - 9.45 u^2 + 17.683 u^3$$

Fit $R^2 = 0.99983$

Alternatively, the (P,u) data can be fitted to a second order polynomial resulting in

$$P^{porous} = 0.1008 u + 3.2257 u^2 - 2.9439 u^3$$

Fit $R^2 = 0.99999$

It is of interest to see what the calculated continuum temperature will be if this 20% porous mixture is shock loaded. The motivation for doing the continuum temperature calculations was to see if they exceed the aluminum oxide melt temperature. This can be done by numerically integrating Eq. 5.50 of reference 6. For the solid mixture shocked to 101 Kb the continuum temperature was calculated to be 503 K and at 316 Kb the temperature is 1,260 K. The 20 % porous mixture for a shock of 104 Kb resulted in a shock temperature of 869 K while for 316 Kb the shock temperature is 2,380 K. These calculated temperatures are considerably below the oxides melt temperature at these pressures which eliminates the idea that the oxide is being melted by the temperature in the mix due to the shock loading. This was the expected result but the calculations needed to be done so this can be said definitely. Therefore, other mechanisms must be active in getting aluminum particles with oxide coatings to react with water under shock loading as reported in the literature.

It is useful to note that the mixture law approach for obtaining the unreacted Al/water Hugoniot above can be used on three metal component mixture's. This is very useful if experimental data does not exist for such reactive metal mixtures unreacted Hugoniot.

Changing reaction kinetics with porosity and/or aluminized micro-balloons

This author has proposed that a good technique for changing the kinetics of the reaction of the porous Al/water samples is to add glass micro-balloons heavily coated with aluminum. SRI International, under a purchase order, coated hollow glass micro-spheres (HGMS) with an aluminum coating that was above 50% of aluminum by weight. They successfully deposited Aluminum metal coating by chemical vapor deposition in a fluid bed reactor on thin glass micro-sphere walls (200-300 nm thick). Each sphere is homogeneously coated with a layer of Al. However, the thickness coated on different spheres could be different, which would be caused by the sticking of some particles on the reactor wall and was later shaken down by applying some vibration.

SRI achieved at least >50% weight gain after coating the HGMS with Al. They used optical microscopes and SEM to characterize the surface morphology of the micro balloons (Fig. 1), also X-ray fluorescence (XRF) to identify the composition of the coating and X-ray diffraction (XRD) to confirm the presence and crystallinity of Al coated on glass, and whether pure Al phase is formed. By optimizing the experimental conditions further, larger batches and much thicker layer of Al on those hollow glass micro-spheres can be produced.

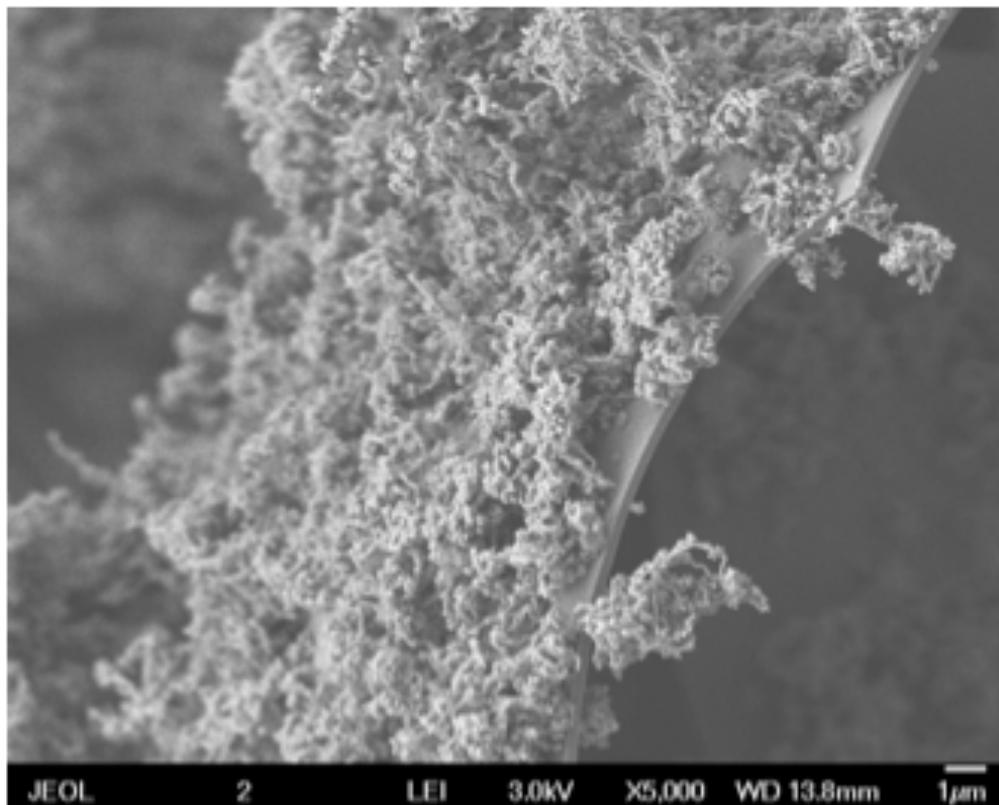


Fig. 1 Hollow Glass sphere coated with Al layer. Micro-balloon was broken to show relative thickness of Al to 0.3 μ glass wall

Shock driver systems to reach the high initiation pressures of the mixture

Note that a direct measurement of reaction rate in such a composite sample has never been made to date. One-dimensional strain shock experiments allows for such a measurement to be made. However, an explosive flyer plate driver system is needed to reach shock pressures above 50 kbar in a 50%/49%/1% by weight of aluminum particle/water/glass micro-balloons. Such a driver system is shown in Fig. 2 where a 2.54 cm thick TNT plate drives a shock wave into a 2.54 cm thick brass plate that has an aluminum flyer on top of the brass plate. Higher pressures can be obtained if an explosive more energetic than TNT is used. However, it has to be assured that the flyer plate does not spall under its shock acceleration.

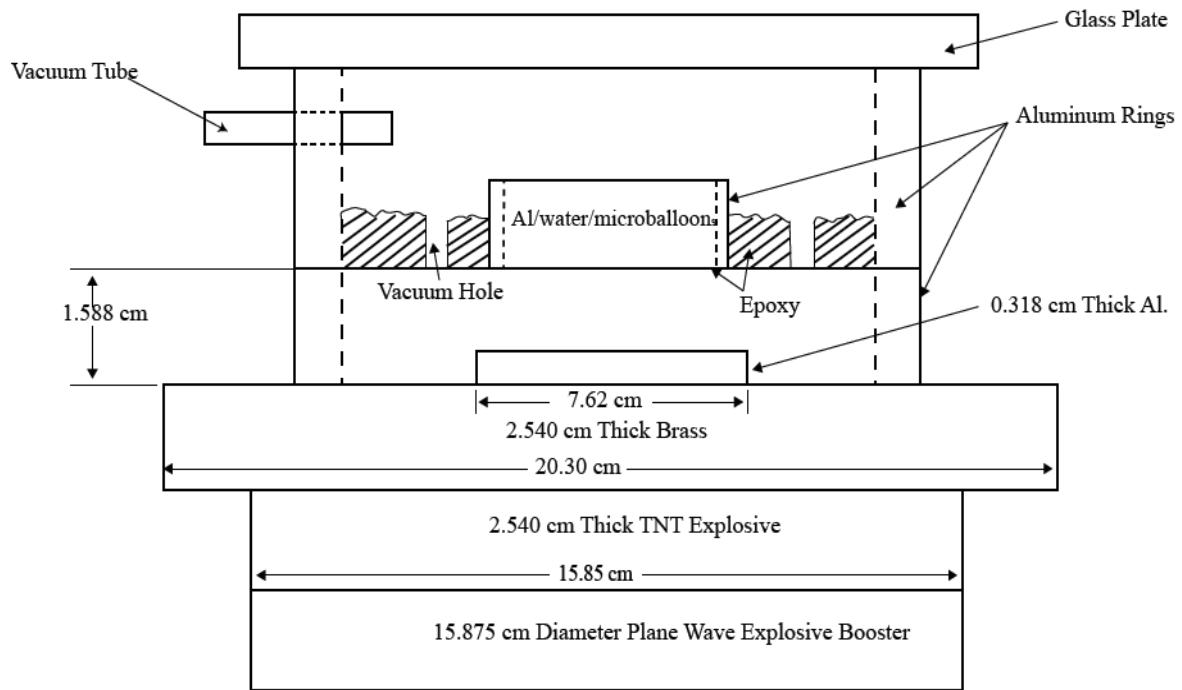


Fig. 2 Explosive flyer plate driver system for achieving 58 kbar

This driver system is similar to the one used to study the phase transition in Armco iron [6]. The aluminum flyer plate is accelerated across a 1.3 cm vacuum gap impacting the Al/water/micro-balloon sample at a velocity of 1.62 mm/ μ s, which would result in a stress of 58 kbar in the 50/50 by wt Al/water composite sample according to the theoretical unreacted mixture Hugoniot developed earlier.

Summary

Baseline unreacted Hugoniots for the Al/water mixtures have been calculated using the kinetic energy averaging equation for mass fractions and the known Hugoniots of each constituent. A very practical way of changing aluminum/water reaction rate under shock loading by adding thick aluminum coated micro-spheres to the mixture was presented. A process to make thick aluminum coatings on glass microspheres was then developed. In addition, the goal of designing a one-dimensional explosively driven flyer plate for shock wave experiments on these composites was done.

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